ABSTRACT: Semiconductor—metal hybrid nanostructures are one of the best model catalysts for understanding photocatalytic hydrogen generation. To investigate the optimal structure of metal cocatalysts, metal−CdSe−metal nanodumbbells were synthesized with three distinct sets of metal tips, Pt−CdSe−Pt, Au−CdSe−Au, and Au−CdSe−Pt. Photoelectrochemical responses and transient absorption spectra showed that the competition between the charge recombination at the metal−CdSe interface and the water reduction on the metal surface is a detrimental factor for the apparent hydrogen evolution rate. For instance, a large recombination rate (k_rec) at the Pt−CdSe interface limits the quantum yield of hydrogen generation despite a superior water reduction rate (k_WR) on the Pt surface. To suppress the recombination process, Pt was selectively deposited onto the Au tips of Au−CdSe−Au nanodumbbells in which the k_rec was diminished at the Au−CdSe interface, and the large k_WR was maintained on the Pt surface. As a result, the optimal structure of the Pt-coated Au−CdSe−Au nanodumbbells reached a quantum yield of 4.84%. These findings successfully demonstrate that the rational design of a metal cocatalyst and metal−semiconductor interface can additionally enhance the catalytic performance of the photochemical hydrogen generation reactions.

KEYWORDS: Nanoparticles, photocatalyst, hydrogen generation, metal cocatalyst, charge recombination

Solar hydrogen generation is an ideal alternative to fossil fuels due to its environmentally clean nature using plentiful resources, sun light, and water.1 To get hydrogen from water at high efficiency, the rational design of photocatalysts is apparently the most detrimental problem.2−5 Among various materials, a hybrid structure of semiconductor and metal components is regarded as an ideal photocatalyst structure in which photoinduced charge separation occurs at the semiconductor domain, and the subsequent electron transfer to the metal leads to efficient hydrogen generation on its surface.6,7 Although metal−semiconductor hybrid catalysts contain only two components, they exhibit sophisticated photophysical kinetics with multiple variables, such as charge separation,8−10 relative band alignment,11,12 hole transfer rate,13−16 and charge recombination during photocatalytic reactions. To address these kinetic issues, semiconducting nanorods decorated with metal tips are one of the best model catalysts because each domain is single-crystalline with a well-defined morphology,18 which induces simple catalytic pathways with effective charge separation through uniform electronic junctions.19 Since Banin et al. reported the selective growth of Au tips on semiconductor nanorods,20 many researchers have tried to carry out accurate kinetic studies on the catalyst structure to understand detailed reaction processes. Among various kinetic factors, recent works

Received: June 19, 2017
Revised: August 10, 2017
Published: August 29, 2017
have particularly focused on charge separation and transfer that mainly occur at the semiconductor domains. For instance, Tang et al. investigated charge separation behaviors on CdSe—metal nanorods and found that Pt completely extracted excited electrons from the CdSe nanorod, but Au could not. Alivisatos et al. demonstrated that effective hole localization on the CdSe cores and the long distance between the CdSe and Pt tips significantly increased the hydrogen production efficiency in a CdSe core/CdS nanorod structure with Pt tips. Lian et al. investigated the trend in hydrogen evolution rates on CdS/Pt and CdSe/CdS—Pt nanorods with respect to their hole transfer rates. The kinetics related to the metal domains and their interfaces are also important; however, these have been rarely investigated thus far. Banin et al. recently reported the importance of the metal tip size on the photocatalytic efficiency. Amirav et al. synthesized metal alloy tips, which greatly changed the catalytic properties on the surface by heterometallic bonding interactions.

In the present work, we chose CdSe nanorods decorated with metals at both tips, usually referred to as nanodumbbells, as a model catalyst for photocatalytic hydrogen generation. In particular, we varied the metal tips, which largely altered the kinetic parameters related to the metal domains and the metal—semiconductor interface and eventually determined the catalytic efficiency. By means of photoelectrochemical measurements and transient absorption spectroscopy, we show that the competition between the charge recombination at the metal—semiconductor interface and the water reduction on the metal surface significantly contributed to the apparent hydrogen production rate. As well as the optimization of the kinetics at the semiconductor domains, a rational tailoring of the metal domains can additionally enhance the catalytic activities of solar hydrogen production.

To fix other structural factors except for the metal tips, Pt—CdSe—Pt and Au—CdSe—Au nanodumbbells were synthesized by modifying the methods according to the literature. In the Pt—CdSe—Pt nanodumbbells, the CdSe nanorods have an average dimension (length x diameter) of 13.6 x 5.0 nm with an average Pt tip size of 3.4 nm. The latter structure has a dimension of 13.0 x 4.6 nm with a Au tip size of 3.4 nm (Figure S1, Supporting Information). In addition, we synthesized asymmetric nanodumbbells with heterometal tips, Au—CdSe—Pt, by the sequential deposition of Pt and Au precursors on the CdSe nanorods, for the first time. After the formation of the Pt—CdSe single-tipped nanorods, the Au precursor solution was added to the particle dispersion in the presence of didodecylidithylammonium bromide (DDAB) and dodecylamine (DDA) in which DDA had a dual role as a surfactant and a reductant. The inverse sequence of the precursor addition did not work at all because an irregular deposition of Au occurred at the CdSe nanorods during the formation of the Au—CdSe single-tipped nanorods through the Ostwald-ripening-like process.

The transmission electron microscopy (TEM) image in Figure 1a shows that both ends of the CdSe nanorods are successfully decorated by tiny metal domains. The CdSe nanorods are uniform with an average length of 12.6 ± 1.5 nm and an average diameter of 4.6 ± 0.3 nm. The average diameters of the Au and Pt tips are 4.4 ± 0.4 nm 3.0 ± 0.3 nm, respectively, for which the positions were identified by elemental mapping (see below). The high-resolution TEM (HRTEM) image of an individual Au—CdSe—Pt nanodumbbell structure shows that each domain is single crystalline with the formation of a well-defined junction with the neighboring domains (Figure 1b). The lattice spacing of the metal domains matches the distance of the Au(200) (0.204 nm) or Pt(111) (0.227 nm) planes, respectively. The elemental mapping images inevitably prove that the Au—CdSe—Pt heterometal nanodumbbells are formed, the two ends of which are clearly distinguished by the Pt (green) and Au (red) elements (Figures 1c—f and S2, Supporting Information). The X-ray diffraction (XRD) data show the patterns from a combination of hexagonal wurtzite CdSe (JCPDS No. 08—0459) and face-centered cubic Pt (JCPDS No. 04—0802) and Au (JCPDS No. 04—0784) (Figure S3).

The UV—visible absorption spectrum of the CdSe nanorods shows a strong absorption peak centered at 635 nm (Figure S4), which is assigned to the first excitonic transition (1v — 1v) from the valence band edge to the conduction band edge in the CdSe. This apparent peak was broadened after the deposition of the Au or Pt on the CdSe nanorods due to the delocalization of the electronic states of the semiconductor into the metal domains. In the photoluminescence spectra, all the nanodumbbells exhibit complete quenching of the signals implying effective electron transfer from the CdSe nanorods to the metal tips (Figure S5). This photophysical feature provides the evidence that the metal tip growth on the semiconductor nanorods develops effective electronic junctions between the metal and the semiconductor domains.

The metal—semiconductor nanodumbbells are excellent model catalysts for hydrogen production from water. To investigate their catalytic properties, three distinct nanodumbbells, Pt—CdSe—Pt, Au—CdSe—Au, and Au—CdSe—Pt, were transferred to aqueous media through surfactant exchange with mercaptoundecanoic acid (MUA). Hydrogen production was induced by the illumination of visible light (λ ≥ 420 nm) in the presence of hole scavengers, Na2SO3 and Na2S. Figure 2 shows
that hydrogen evolution continuously occurs along the reaction progress for all catalysts; however, the evolution rate is highly dependent upon the metal component. After a 2 h irradiation, the amount of hydrogen production was on the order of Au−CdSe−Pt (61 μmol) > Pt−CdSe−Pt (30 μmol) > Au−CdSe−Au (6.0 μmol). The quantum efficiency was estimated to be 2.45% for Au−CdSe−Pt, 1.55% for Pt−CdSe−Pt, and 0.22% for Au−CdSe−Au, respectively, by irradiation from a light emitting diode at 420 nm (see Supporting Information).

In general, Pt is known as the best cocatalyst for photocatalytic hydrogen generation due to its favorable proton binding energy,1,2 and low electrochemical impedance facilitating electron diffusion into the surface-adsorbed species.2,26 In the case of junction formation with semiconductors, Pt completely extracts electrons from the semiconductor and transfers them to the surface adsorbed species, but Au cannot.9 Based on these properties, it is easy to propose that the Pt−CdSe−Pt may facilitate electron transfer more efficiently than that of the others due to the existence of the double Pt tips. In this regard, the present twice larger activity of the Au−CdSe−Pt nanodumbbells compared to that of the Pt−CdSe−Pt is totally unexpected. It indicates that the electron transfer rate through metal cocatalysts is not the only critical factor dominating the apparent reaction activity.

To investigate the photocatalytic properties in detail, the photoelectrochemical responses of the nanodumbbells were examined. The catalysts were drop-casted onto a SnO2/ITO plate, and the resulting electrode was used as a working electrode in a three-electrode photoelectrochemical cell (see Supporting Information). The resulting nanodumbbell films on the electrodes had the thicknesses of 35 nm and showed nearly identical optical behaviors to the CdSe films (Figure S6, Supporting Information). A current−time response curve was measured at an applied potential of −0.5 V versus Ag/AgCl under visible light irradiation (λ ≥ 420 nm) (Figure 3a). By the irradiation of light, electrons are excited to the conduction band edge of the catalyst generating photocurrents. Photogenerated holes are simultaneously transferred to the hole scavengers, Na2SO3 and Na2S, in the aqueous medium. The hole transfer efficiency in this cell is considered to be 100% due to the fast kinetics at the electrode−medium interface.27 The photocurrent densities of the bare and Pt-tipped CdSe nanorods tend to decrease due to the increase in the number of metal tips (CdSe (−0.105 mA/cm²) > CdSe−Pt (−0.079 mA/cm²) > Pt−CdSe−Pt (−0.058 mA/cm²))). Moreover, it is clearly dependent upon the metal tip composition of the nanodumbbells on the order of Au−CdSe−Au (−0.068 mA/cm²) > Au−CdSe−Pt (−0.062 mA/cm²) > Pt−CdSe−Pt (−0.058 mA/cm²). The smaller photocurrent density in the presence of the metal tips is attributed to electron−hole recombination at the metal−semiconductor interface.28 In particular, the distinct decrease of the photocurrent by increasing the number of Pt tips compared to that of the Au tips indicates that the recombination rate at the Pt interface is larger than that at the Au tips (see below for krec). The action spectra in Figure 3b show that all the catalysts exhibit absorption patterns in the range of 300−700 nm similar to that of the bare CdSe nanorods.29 In these spectra, the increase in the number of Pt tips leads to a decrease in the absorption intensity, also indicating that facile charge recombination occurs at the Pt−CdSe interface.

Transient absorption (TA) spectroscopy is an excellent measurement that can provide kinetic information on the charge carrier dynamics. TA was measured after photoexcitation by pump pulses at 400 nm with a laser fluence of 30 nJ/pulse. The TA spectra of the nanodumbbells exhibit a strong negative absorption peak at 635 nm due to the state filling of the first excitonic transition (σg → σg), and
Figure 4. (a) Transient absorption spectra of Au−CdSe−Pt nanodumbbells with time delays after 400 nm excitation. (b) Normalized TA time traces and fits (black) of Pt−CdSe−Pt (blue), Au−CdSe−Pt (red), and Au−CdSe−Au nanodumbbells (green) after 400 nm excitation with a laser fluence of 30 nJ/pulse. (c) Energy band alignment diagram with available kinetic routes at pH 13. (d) Measured rate constants and calculated quantum yield of Pt−CdSe−Pt, Au−CdSe−Pt, and Au−CdSe−Au nanodumbbells. *From ref 31.

The short lifetime in the Pt-tipped nanodumbbells indicate that the charge recombination rate at the Pt tips is larger than that of the Au tips.

Based on the experimental results for the hydrogen evolution reactions, photoelectrochemical responses, and transient absorption spectra, the photophysical behaviors are rationalized using a kinetic model shown in Figure 4c.8 All energy levels in the scheme are adjusted with respect to our experimental conditions at pH 13. The morphology of the nanodumbbells, including the size of the CdSe and metal domains and their interface structure, is essentially uniform, which renders the kinetic model simple with less kinetic parameters. The photogenerated electrons either directly undergo recombination with the holes on the CdSe domain (with a rate of $k_{rec}$) or are transferred to the metal tips (with $k_{ET}$). The electrons on the metal domain either proceed via the water reduction reaction on the surface (with $k_{WR}$) or are recombined with the holes at the interface region (with $k_{ST}$). The photogenerated holes are trapped with a rate of $k_{ST}$, which is relevant to the electron transfer kinetics.8 According to this simplified kinetic model, the efficiency of the hydrogen evolution reactions can be derived with the following eq (Supporting Information):

$$QY = \frac{k_{ET}k_{WR}}{(k_{WR} + k_{rec})(k_{ET} + k_{ST} + k_{h,k})}$$

In this equation, the electron−hole recombination rate ($k_{h,k}$) is known to be very slow ($\tau = 4.9$ ns for CdSe) compared to the other processes.53,34 The hole trapping rate ($k_{ST}$) is estimated to be 0.14 ns$^{-1}$ ($\tau = 7$ ns) in the CdSe nanorods, for which the rate negligibly changed after the metal deposition.51 The electron transfer rates to the metal tips ($k_{ET}$) on all the
nanodumbbells are estimated in the magnitude of ps⁻¹ from the lifetimes of the bleached signals (τ₁) in the TA spectra. If we accept these values, kₖₑₜ is much larger than kₑₛ and kₛₜ, and eq 1 can be further simplified by kₑₜ + kₛₜ + kₑₛ ≡ kₑₜ as follows:

\[
\text{QY} = \frac{k_{\text{WR}}}{k_{\text{WR}} + k_{\text{rec}}}
\]

(2)

This equation means that the competition between the charge recombination at the metal–semiconductor interface (with kₑₛ) and the water reduction reaction on the metal surface (with kₚₖₑₜ) is critical to determine the quantum yield of the catalytic system. Using eq 2, all rate constants in this kinetic model, kₑₜ, kₑₛ, and kₑₛ are quantitatively analyzed from the quantum yields measured by the experiments (Figure 4d).

As we expected from the photocurrent generation data, the kₑₛ of the Au–CdSe–Au dumbbells is at the minimum, although the quantum yield of the hydrogen generation is the lowest due to the significantly low value of the kₑₛ. In contrast, both the kₑₛ and kₑₛ are large in the Pt–CdSe–Pt and Au–CdSe–Pt dumbbells, and the kₑₛ mainly influences the quantum yields. It is very difficult to extract the contribution of each metal tip (either Au or Pt) on these double-tipped structures, but it is clear at least that the number of Pt tips tends to largely increase the kₑₛ, resulting in the relatively low quantum yield of the Pt–CdSe–Pt compared to that of the Au–CdSe–Pt. The decrease in the quantum yield by recombination losses was similarly reported in multiple Pt clusters on CdS nanorods.²⁷

It is noted that the kₑₛ of the Au–CdSe–Pt is even larger than the kₑₛ of the Pt–CdSe–Pt, although the latter structure has multiple Pt tips. Amirav et al. found that a single catalytic site per excitation unit is statistically advantageous to form all intermediates on the same catalytic site in multielectron reactions.³⁴ Pt has a far lower H⁺ chemisorption energy than Au²² so that all reaction intermediates majorly form at the Pt sites, as similarly occurred in single Pt-tipped nanorods. In regard to the electron transfer, Au has a tendency to store electrons without transferring them to the surrounding media,¹²,³⁶ which promote the electron transfer toward the Pt tips. These factors may induce the high value of the kₑₛ in the Au–CdSe–Pt nanodumbbells. For the single Pt-tipped CdSe nanorods, the amount of hydrogen production was measured to be 140 μmol by a 2 h irradiation of visible light (Figure S8, Supporting Information), which was much larger than that of the Au–CdSe–Pt nanodumbbells. This high activity cannot be directly compared to those of the nanodumbbell structures, due to superior hole transfer to the sacrificial reagents through the open ends.¹⁰,²³ The charge recombination rate at the interface is also the lowest as shown in Figure 3a.²⁷ However, it still indicates that the smaller number of active cocatalyst per catalyst unit is essential to enhance the photocatalytic activity.³⁵

The findings in our experiments provide intuition for the rational design of a metal cocatalyst with high efficiency; i.e., the suppression of kₑₛ as well as the enhancement of kₑₛ. The Pt tips induce a high kₑₛ but also a high kₑₛ whereas the Au tips exhibit a very low kₑₛ but also a low kₑₛ in the nanodumbbell structure. Apparently, the hybridization between the low kₑₛ of the Au domains and the high kₑₛ of the Pt surface would be able to maximize the total catalytic performance. The resulting design is a Pt coating on the surface of the Au tips in the Au–CdSe–Au nanodumbbells. In this structure, the low kₑₛ is conserved at the Au–CdSe interface, and the Pt surface coating on the Au tips would significantly increase the kₑₛ (Figure 5). To synthesize the Pt-
coated Au−CdSe−Au nanodumbbells, the Pt precursor was added to the Au−CdSe−Au dispersion in oleylamine at high temperature. Figure 5a shows that the dumbbell structure is well maintained after the Pt deposition. The energy dispersive X-ray spectroscopic analysis indicates that the product contains 7.6 atomic % Pt. Elemental mapping of an individual nanodumbbell also shows that Pt selectively coats the surface of the Au tips, but not the CdSe wall (Figures 5b–d). Nearly all Au tips of the nanodumbbells are coated with the Pt layers (Figure S9, Supporting Information). As shown in Figure 5e, the hydrogen evolution rate under the present reaction conditions remarkably increases as we expected; for a 2 h irradiation of visible light, the amount of hydrogen generation was measured to be 125 μmol, which is tremendously increased from the uncoated Au−CdSe−Au (6.0 μmol) and is even twice larger than that of the Au−CdSe−Pt (61 μmol). This value is also comparable to that of the single tipped Pt−CdSe, although the number of metal tips per a single catalyst unit is twice. The quantum yield of the Pt-coated Au−CdSe−Au reached 4.84%, which is also superior to the other nanodumbbells. A similar bimetallic approach with Pt and Au was reported in CdSe@CdS nanorods in which the authors proposed that the exposed interfaces between the Pt and Au are a key factor. In our catalysts, the photochemical response shows that the photocurrent of the Pt-coated Au−CdSe−Au nanodumbbells is identical to that of the original Au−CdSe−Au nanodumbbells, implying that the recombination rate at the Au−CdSe interface does not change during the Pt coating process (Figure 5f). The lifetime ($\tau_3$) of the third decay in the TA spectrum was measured as 38.86 ns, which is also comparable with Au−CdSe−Au (45.74 ns). Consequently, the selective Pt coating at the Au tips largely enhances the $k_{\text{WR}}$ without damaging the $k_{\text{rec}}$ of the original Au−CdSe−Au nanodumbbells.

In conclusion, we synthesized metal−semiconductor nanodumbbells with three distinct sets of metal tips, Pt−CdSe−Pt, Au−CdSe−Au, and Au−CdSe−Pt, all with an identical morphology and size. The photocatalytic activity and quantum yield in the hydrogen evolution reaction are on the order of Au−CdSe−Pt > Pt−CdSe−Pt > Au−CdSe−Au. However, the photocurrent generation follows the order of the number of Au tips, which reveals a low recombination rate at the Pt−CdSe interface compared to that at the Pt−CdSe interface. The results of the transient absorption experiment show that the competition between the charge recombination at the metal−CdSe interface and the water reduction on the metal surface is critical in determining the quantum yield. Based on these findings, we successfully demonstrate that the Pt-coated Au−CdSe−Au nanodumbbell is an optimized catalyst structure bearing a low charge recombination rate and a high water reduction rate at the same time, resulting in a quantum yield reaching 4.84%, which is twice larger than the value of the Au−CdSe−Pt and 40 times larger than that of the original Au−CdSe−Au nanodumbbells. As well as the optimization of the hole transfer kinetics, the rational design and precise engineering of the electron transfer kinetics of the metal cocatalyst and metal−semiconductor interface can further enhance the catalytic performances of photochemical hydrogen generation reactions.

**REFERENCES**
